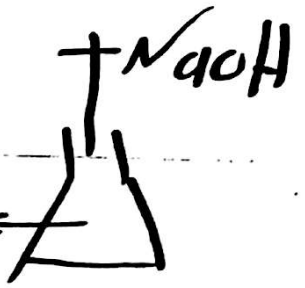
Potentiometry
Phosphoric Acid

SH

* H_3PO_4 Can be Titrated with NaOH by TWO steps Not three steps :-



① $NaOH + H_3PO_4 \overset{K_1}{\rightleftharpoons} NaH_2PO_4$

② $NaOH + NaH_2PO_4 \overset{K_2}{\rightleftharpoons} Na_2HPO_4$

③ $NaOH + Na_2HPO_4 \overset{K_3}{\rightleftharpoons} Na_3PO_4$

$K_1[H^+] \gg 10^{-8}$ very fast Reaction

$K_2[H^+] \gg 10^{-8}$ very fast Reaction

$K_3[H^+] < 10^{-8} \simeq 10^{-12}$ slow step

$\frac{K_1[H^+]}{K_2[H^+]} > 10^4$ fast steps

$\frac{K_2[H^+]}{K_3[H^+]} < 10^4$ slow step.

So occur into two steps

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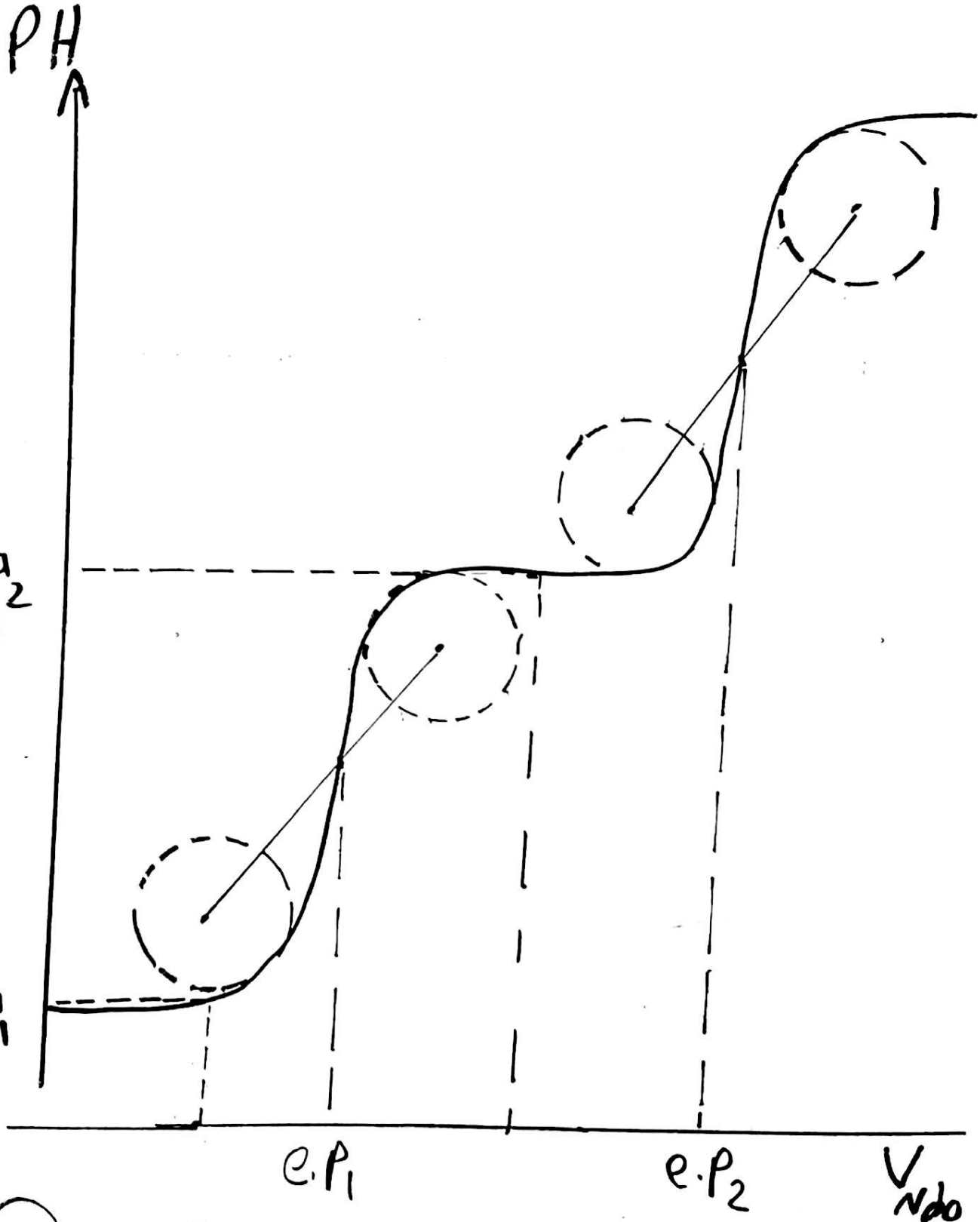
* Potentiometric Curve



Note / $PKa_1 = \frac{1}{2} e.P_1$ / $PKa_2 = \frac{e.P_1 + e.P_2}{2}$

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*First dissociation Constant

$PKa_1 = PH = PK_1 = (Number)$

$K_1 = \log^{-1}(Number)$

*second dissociation Constant

$PKa_2 = PH = PK_2$

$K_2 = \log^{-1}(Number)$

*PK_1 : Middle the distance of e.P_1

*PK_2 : Middle the distance between e.P_1 and e.P_2

* PK_1, PK_2 : Performe Rate of Reaction in which the Reaction fast or slow

— — — — —

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*/ If the Concentration H_3PO_4 by (Normality)

/at e.P1/ $(N.V)_{NaOH} = \frac{1}{3}(N.V)_{H_3PO_4}$

/at e.P2/ $(N.V)_{NaOH} = \frac{2}{3}(N.V)_{H_3PO_4}$

*/ If the Concentration by Molarity/

/at e.P1/ $(M.V)_{NaOH} = (M.V)_{H_3PO_4}$

/at e.P2/ $(M.V)_{NaOH} = 2(M.V)_{H_3PO_4}$

$$\text{eqwt } H_3PO_4 = \frac{M.wt}{3} \longrightarrow (1)$$

$$N = \frac{wt}{eqwt} \cdot \frac{1000}{V} \longrightarrow (2)$$

$$M = \frac{wt}{M.wt} \cdot \frac{1000}{V} \longrightarrow (3)$$

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$$M = \frac{wt}{M.wt} \cdot \frac{1000}{V}$$

$$N = \frac{wt}{eqwt} \cdot \frac{1000}{V}$$

$$N = \frac{wt \times 3}{M.wt} \cdot \frac{1000}{V}$$

$$\boxed{N = 3M}$$

Confirmation of e.P1 and e.P2

* Titration Curve between $\frac{\Delta PH}{\Delta V}$ and the volume of NaoH added

⇒ ΔPH: diffrence between PH in each Reading

⇒ ΔV: diffrence in volume added (equals)

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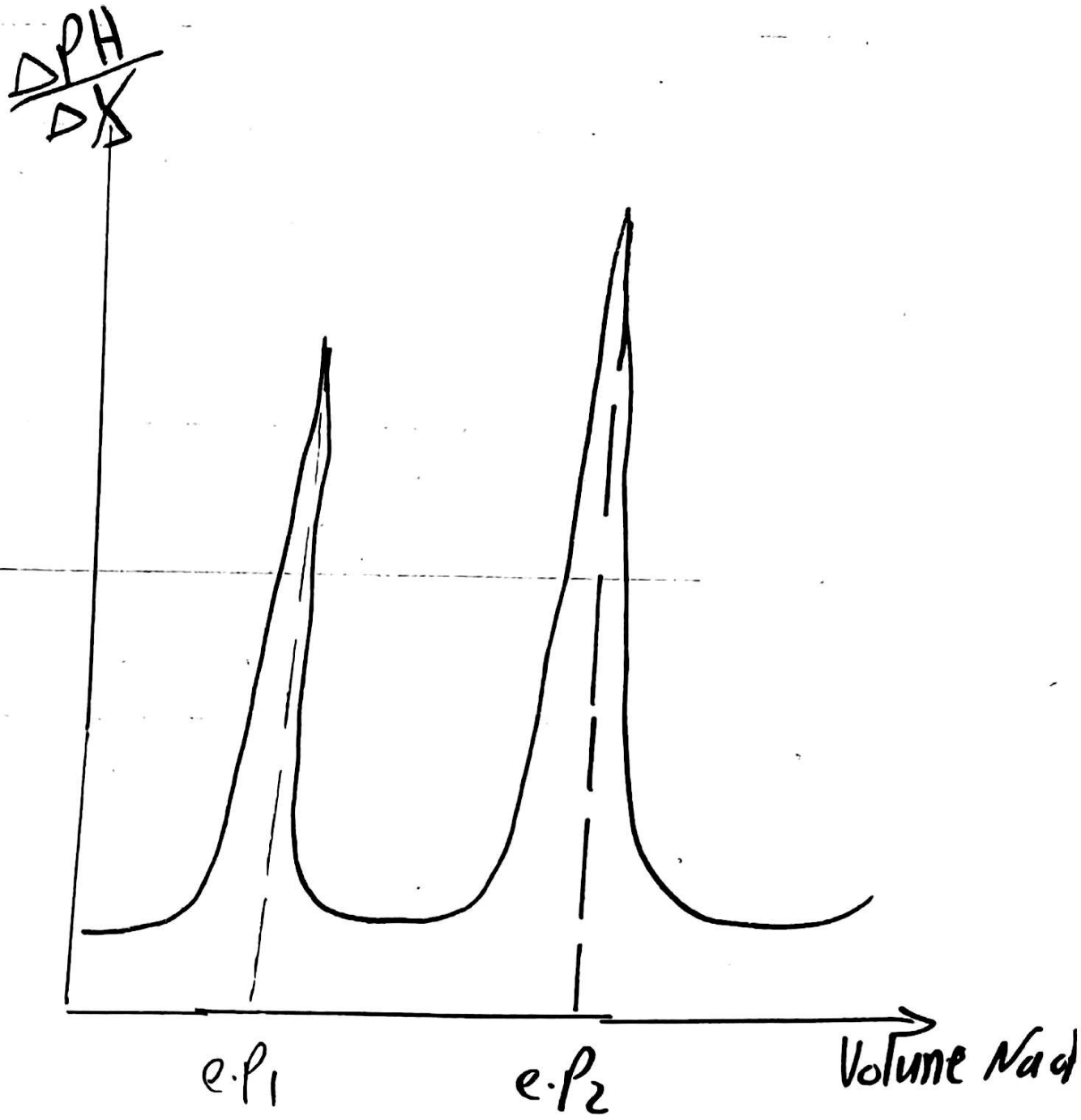

/e.P1/ and /e.P2/ must equals in Titration

The Potentiometric Curve

/Good luck/

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Conductometric Titration

Conductivity: it's the Mobility of Ions in The solutions and it's Reciprocal of specific Resistance of solution.

$$R = \rho \cdot \frac{l}{A}$$

$$\rho = \frac{R \cdot A}{l}$$

$$\rho = \frac{\text{Resistance}(\Omega) \times \text{Area}(cm^2)}{cm(\text{distance})}$$

$\rho : \Omega cm$

$$\text{Conductivity}(K) = \frac{1}{\rho} \quad (\Omega^{-1} cm^{-1})$$

& Unit of Conductivity (K) : $\Omega^{-1} cm^{-1}$)

— — — —

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* factors affecting on Conductivity

① Concentration of solution

by increasing Conc of solution The Mobility of Ions decrease Conductivity decrease

EX / 0.82 M NaOH / 0.1 M NaOH /

0.82 M NaOH : law Conductivity

0.1 M NaOH : high Conductivity

② size of Ions

by increase size of Ions decrease Mobility decrease Conductivity.

EX / Na^+ less in Conductivity than H^+ /

③ Mobilty of Ions

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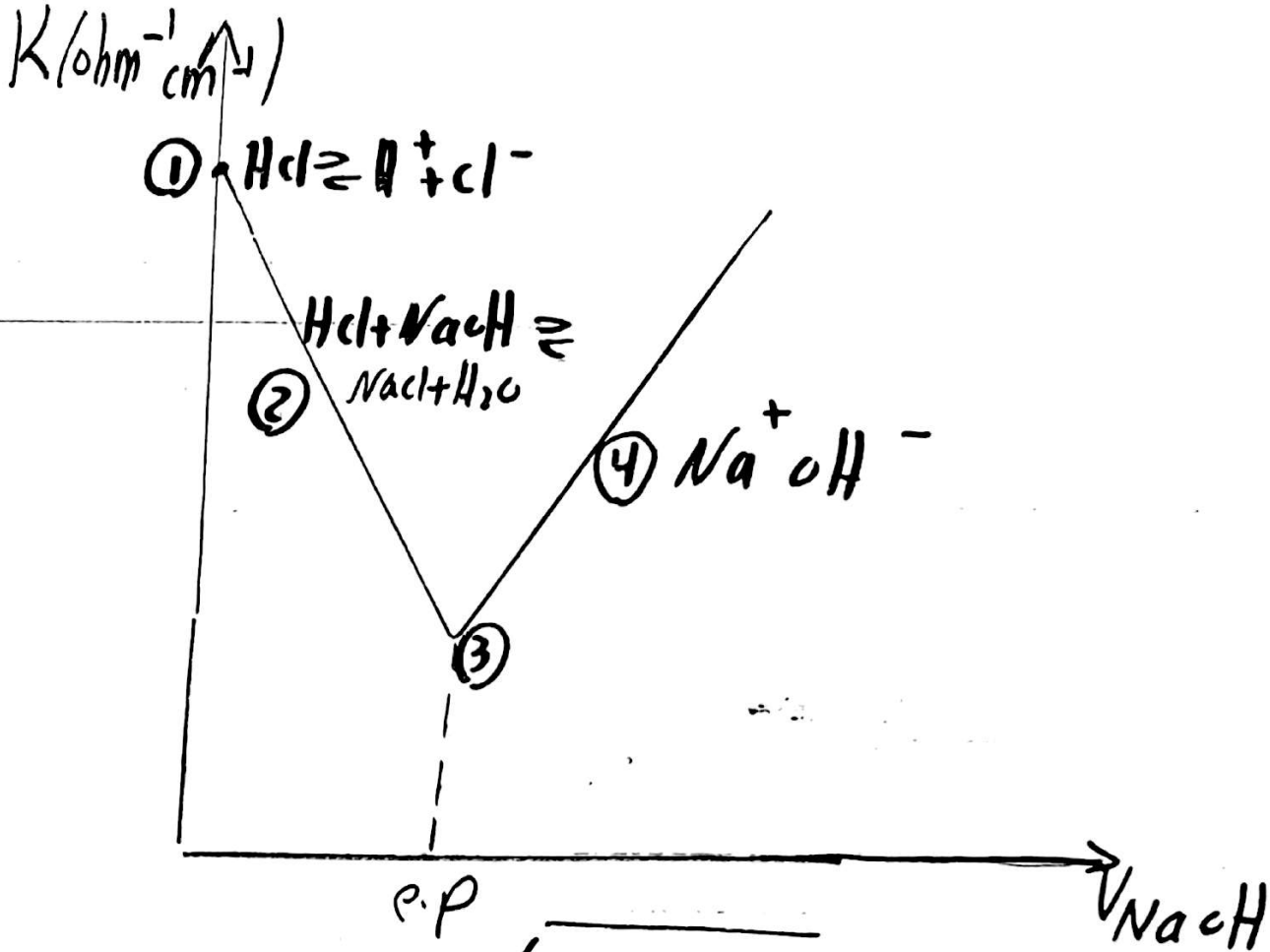
* Determination Conductivity (Normality) of Hcl by NaoH.



Comment

① Hcl (strong electrolyte) ionized Completely to H^+, cl^- in which H^+ (high amount) So Conductivity increase.

② by adding NaoH React with Hcl in which H^+ Replaced by Na^+ so Conductivity decrease

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Due to Na^+ More size than H^+

$\underline{HCl + NaOH \rightleftharpoons NaCl + H_2O}$

③ by adding NaOH all of Hcl finished then Determine e.P.

④ by adding NaOH the Conductivity increase due to Not found Acid (only Na^+, OH^-).

Determine Normality CH_3COOH by NaOH

① CH_3COOH (Partially Ionized): (Weak electrolyte ionized to H^+, CH_3COO^- in which H^+ (law amount) decrease Conductivity) (law Conduc,

② Stage of Comm.on Ion affect in which CH_3COONa dissociate to CH_3COO^-, Na^+

(V)

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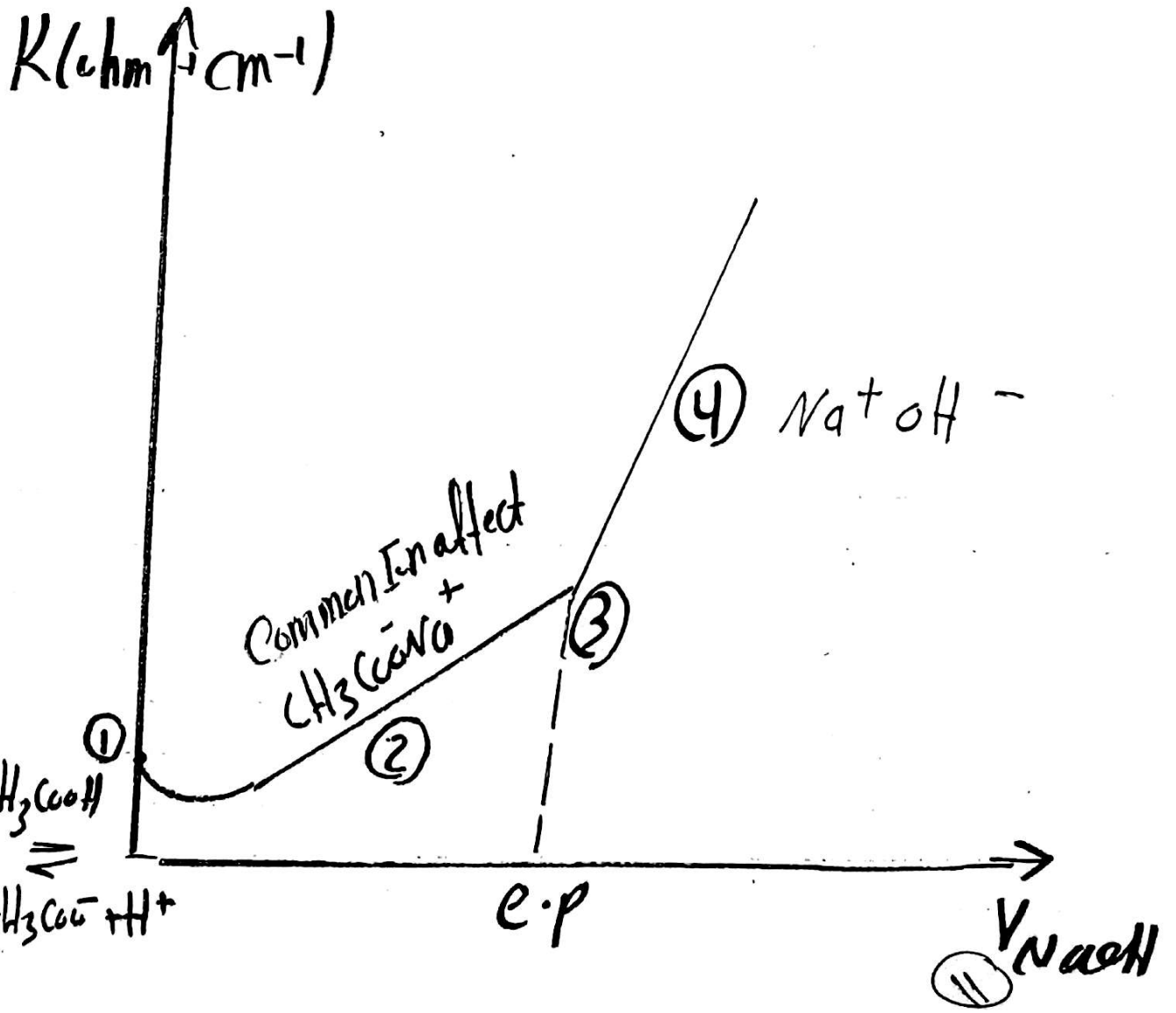
So there are Common Ion affect of acetate that slightly increase or constant Conductivity

③ by adding NaOH all acetic acid finish Then Determine e.p

④ by adding NaOH all (Na^+, OH^-) the Conductivity increase.



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① $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

② $CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$

$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Common Ion effect

Determine of mixture (HCl + NaOH)

① HCl (strong electrolyte) completely ionized to H^+, Cl^- in which H^+ (high amount) increase conductivity

② by adding NaOH React with Hd in which The conductivity decrease due to Replaced H^+ by Na^+ (Na^+ less conductivity than H^+ due to high size of Na^+ than H^+).

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(3) add NaOH till all HCl finished Determ the e.P1

(4) stage of Common Ion effect in which CH_3COONa dissociate to (CH_3COO^-, Na^+) and CH_3COOH ionized to (CH_3COO^-, H^+) so will found Common Ion effect of acetate (increase slightly or Constant Conduct)

(5) add NaOH Till all CH_3COOH finished (e.P2)

(6) add NaOH the Conductivity increase due to found Na^+, OH^- only.

ans

at e.P1

$$(N.V)_{NaOH} = (N.V)_{HCl}$$

at e.P2

$$(N.V)_{NaOH} = (N.V)_{HCl} + (N.V)_{CH_3COOH}$$

(A)

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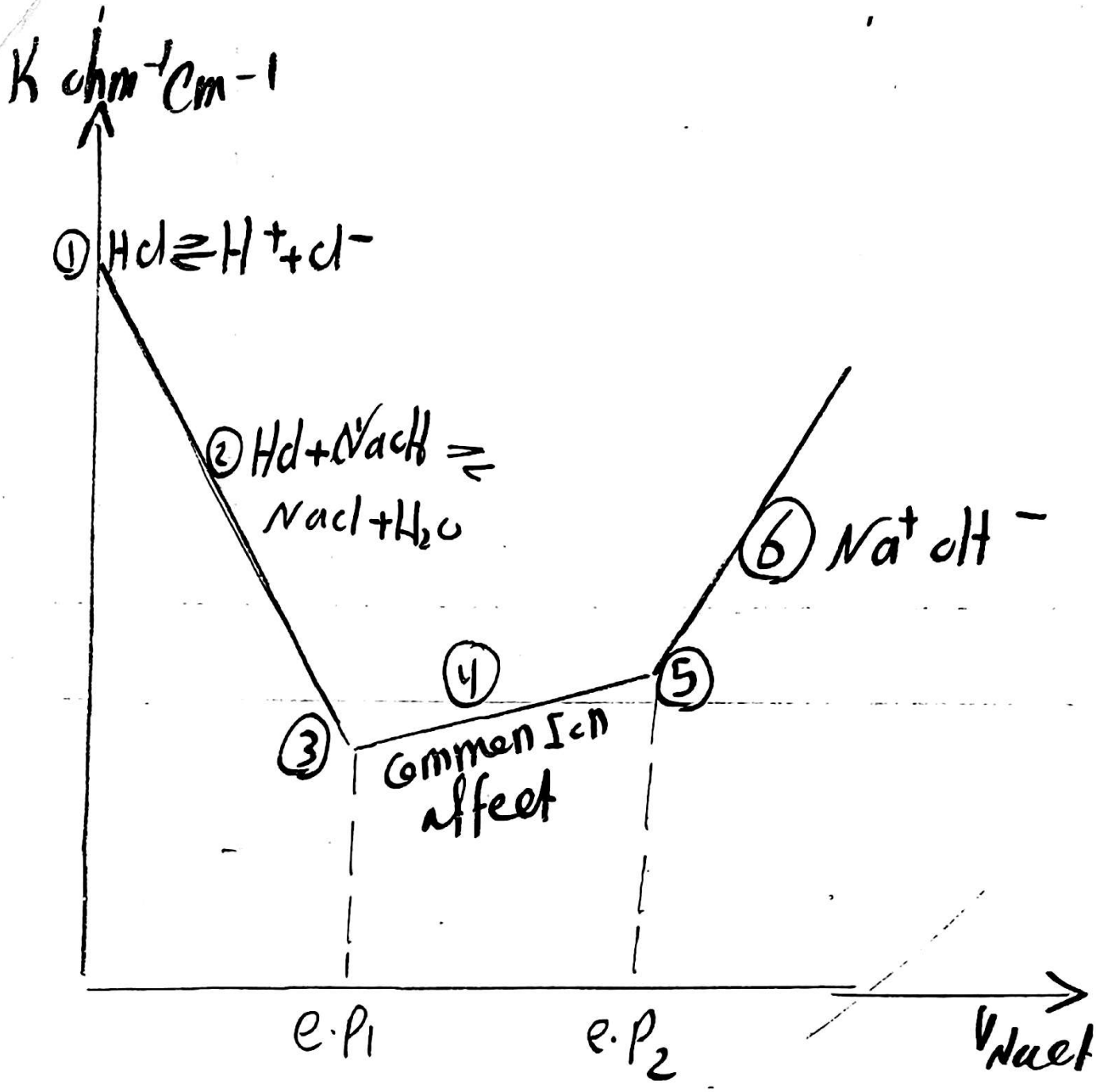

Determine Hd by NHuOH

① Hcl (strong electrolyte) ionized to H^+, Cl^- in which H^+ high amount increase conductivity.

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(2) By add NH_4OH React with Hcl in which H^+ Ref by NH_4^+ in which Conductivity decrease due to NH_4^+ More size than H^+

$$NH_4OH + HCl \rightleftharpoons NH_4Cl + H_2O$$

(3) Add NH_4OH Till all Hcl finished Det e.p

(4) Add NH_4OH the Conductivity Constant Not increase due to NH_4OH (Weak base) weak electrolyte Not abble to increase Conductivity (in which Dissociate to NH_4^+, OH^-) and amount of NH_4^+, OH^- very small Not increase Conductiv

$$(N.V)_{NH_4OH} = (N.V)_{Hcl}$$

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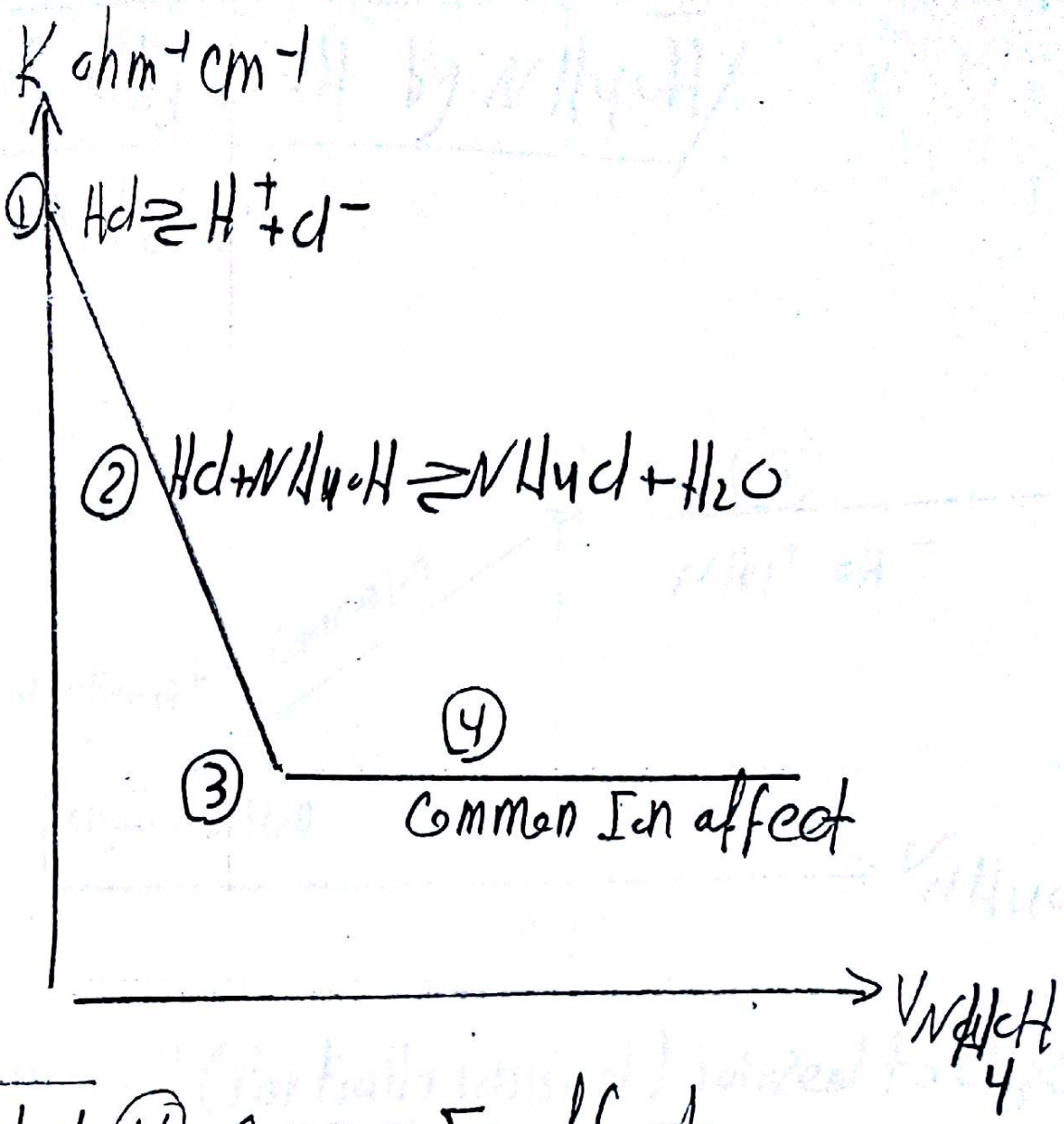

Note/ ④ Common Ion affect

$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

fix conductivity.

Cup luck

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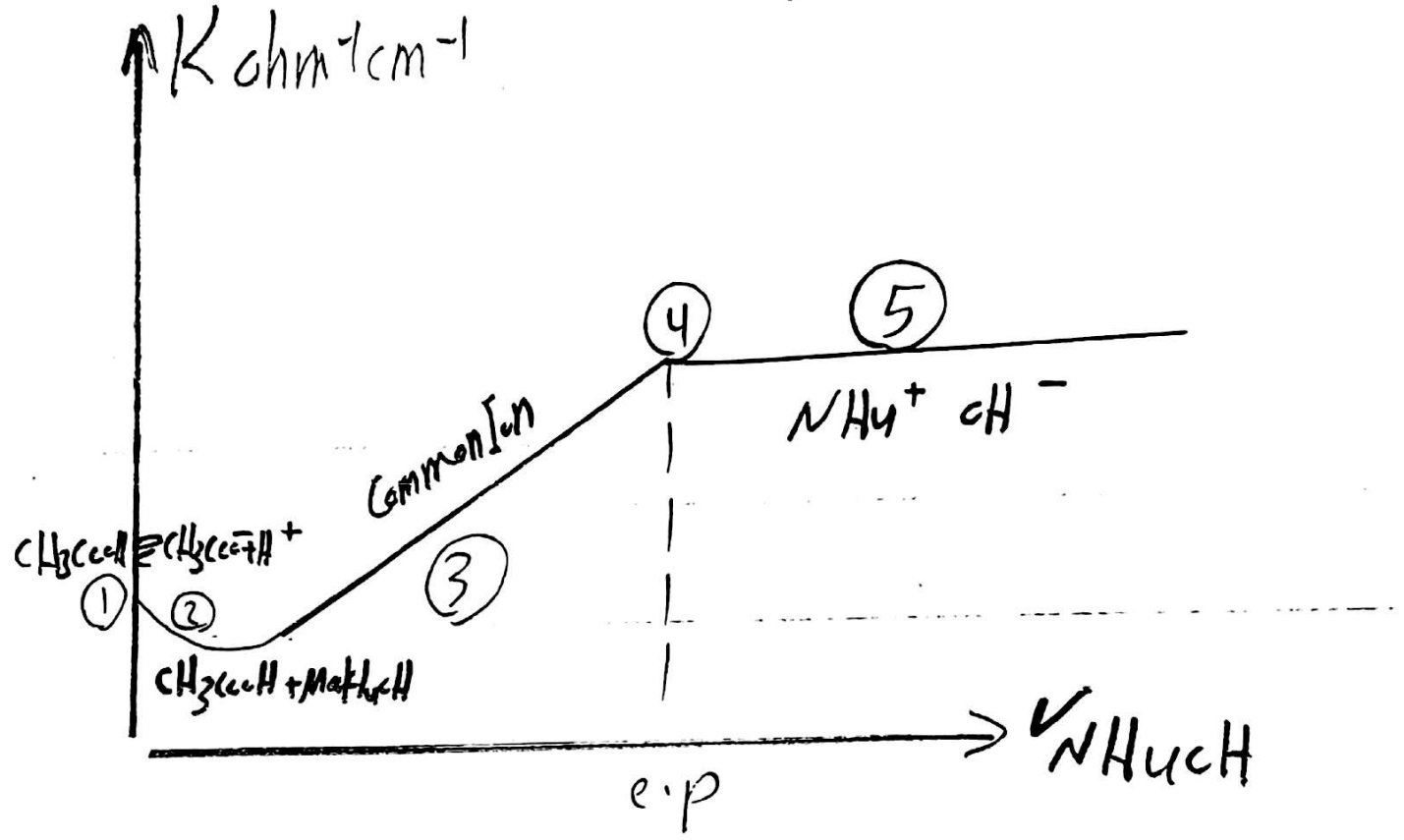
Det CH_3COOH by NH_4OH



① CH_3COOH (Partially ionized) ionized to CH_3COO^-, H^+ amount of H^+ (low) due to CH_3COOH (weak electrolyte) the Conductivity small.

② add NH_4OH React with CH_3COOH in which H^+ Replaced by NH_4^+ the Conductivity decrease due to NH_4^+ high size than H^+.

③ stage of common Ion effect.

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inwhich CH_3COONa dissociate to CH_3COO^-, Na^+ and CH_3COOH Ionized to CH_3COO^-, H^+ so there are Common Ion for CH_3COO^- that increase slightly Conductivity.

④ add NHyOH till all CH_3COOH finish Det e.P

⑤ add NHyOH the Conductivity fix due to NHyOH weak base (amount of NH_4^+, OH^-) small that fix Conductivity.

Det mixt (HCl + CH_3COOH) by NHyOH

at e.P1

$$(N.V)_{NHyOH} = (N.V)_{HCl}$$

at e.P2

$$(N.V)_{NHyOH} = (N.V)_{HCl} + (N.V)_{CH_3COOH}$$

(1)

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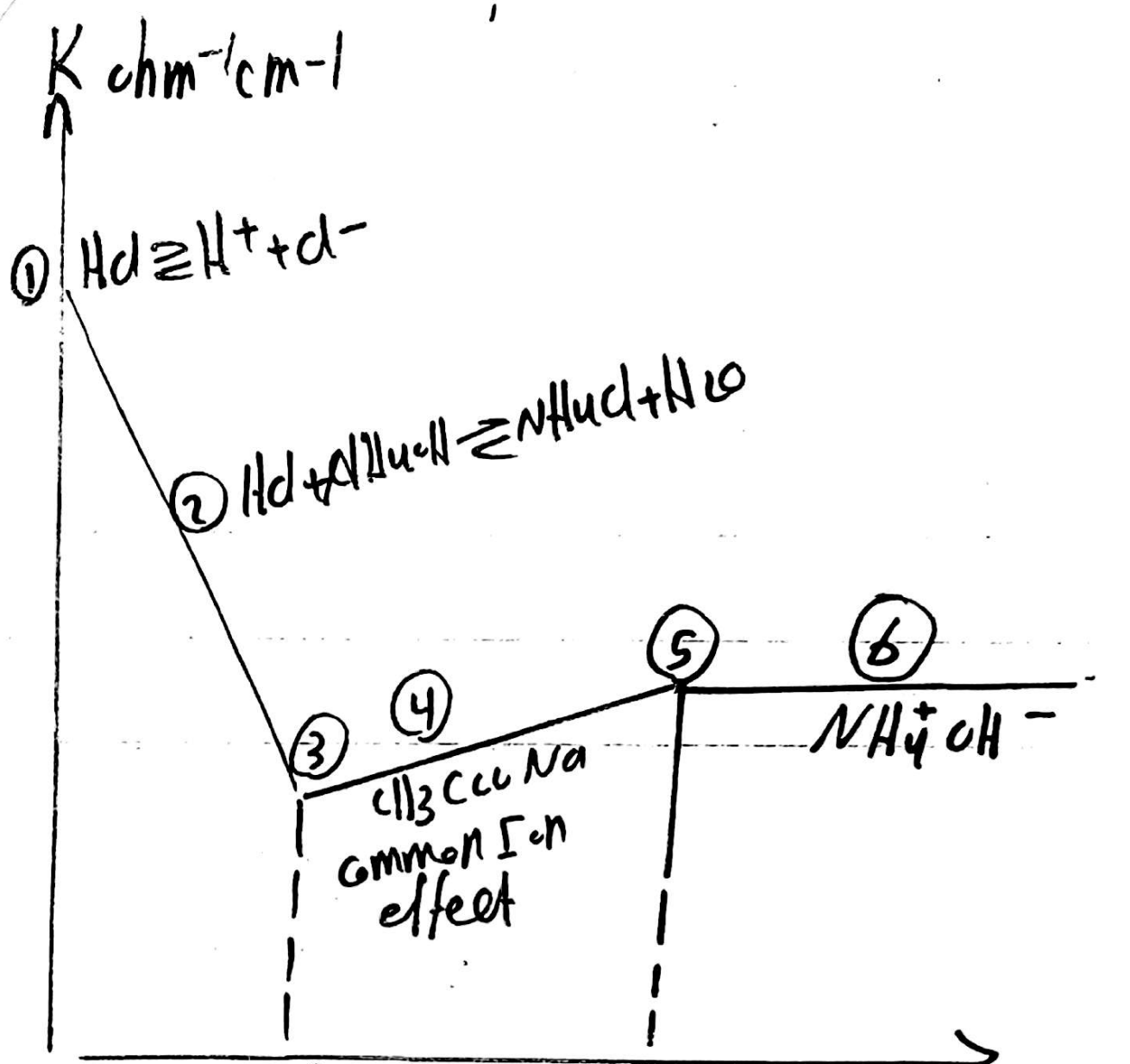

Good luck

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Heating, Cooling Curve

* We study the character of any substance by Phase Rule Cource as ($CH_3COONa \cdot 5H_2O$).

* This substance have Phase character in which we study :-

① Number of (degree of freedom)

Free of substance in Phases (liquid, solid)

② solidification Temp (Solidification Temp)

it's intermediate between Two Phases (Liquid, solid) for any substance as $CH_3COONa \cdot 5H_2O$

③ Super Cooled State

it's the state in which liquid state Convert to Solid state for $CH_3COONa \cdot 5H_2O$.

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* How To Calculate degree of freedom (F) for any substance :-

$$F = C - P + 1$$

C: Number of Component.

P: Number of Phases (liquid, solid, gas).

EX / $CH_3COONa + NaCl$ in liquid state /

$f = C - P + 1$

$f = 2 - 1 + 1$

$F = 1 + 1 = 2$

$C = 2$

$P = 1$

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* / M.wt for sodium acetate /

$CH_3COONa \cdot 5H_2O$

must inter the water in calculation.

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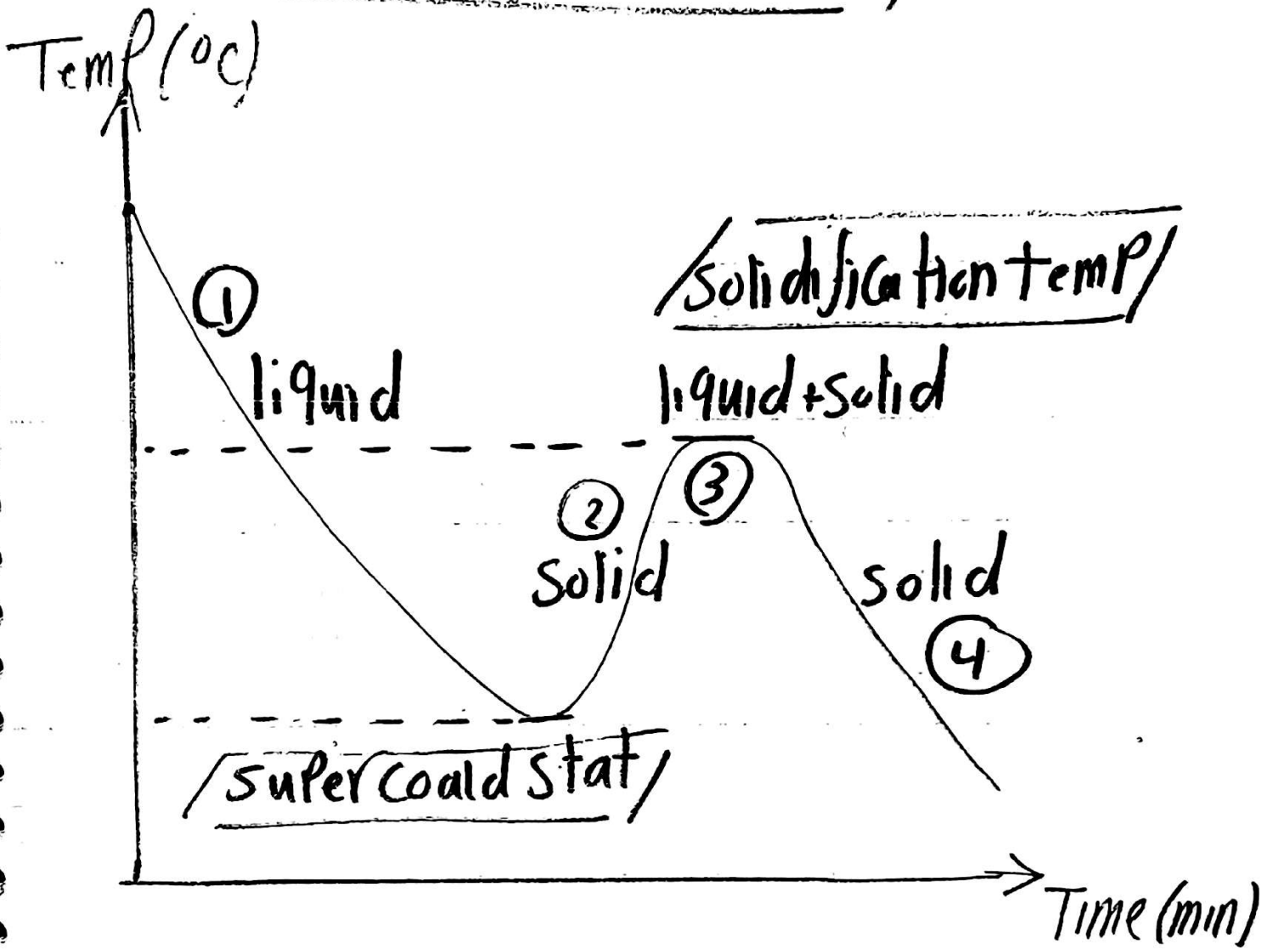
Heating. Cooling curve



① $f = C - P + 1$

$f = 1 - 1 + 1 = 1$ (C=1, P=1)

② $f = 1$ (C=1, P=1)

③ $f = 0$ (C=1, P=2)

④ $f = 1$ (C=1, P=1)

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(EXP 1) Conductimetric Titration

Procedure

① Determine Normality for (CH_3COOH and HCl) by Conductimetric titration.

[1] Add 10 ml mixture ($HCl + CH_3COOH$) in Beaker.
[2] Measure the Conductivity ($K\ ohm^{-1}cm^{-1}$).
[3] Add NaOH (0.1 M) [1ml from NaOH] then Measure Conductivity.
[4] Add 2ml NaOH then Measure Conductivity.
[5] Add NaOH till 40 ml from NaOH then finished.
[6] Draw the curve then Determine Normality of mixture.

Note 10ml mixture + 90ml dist H_2O

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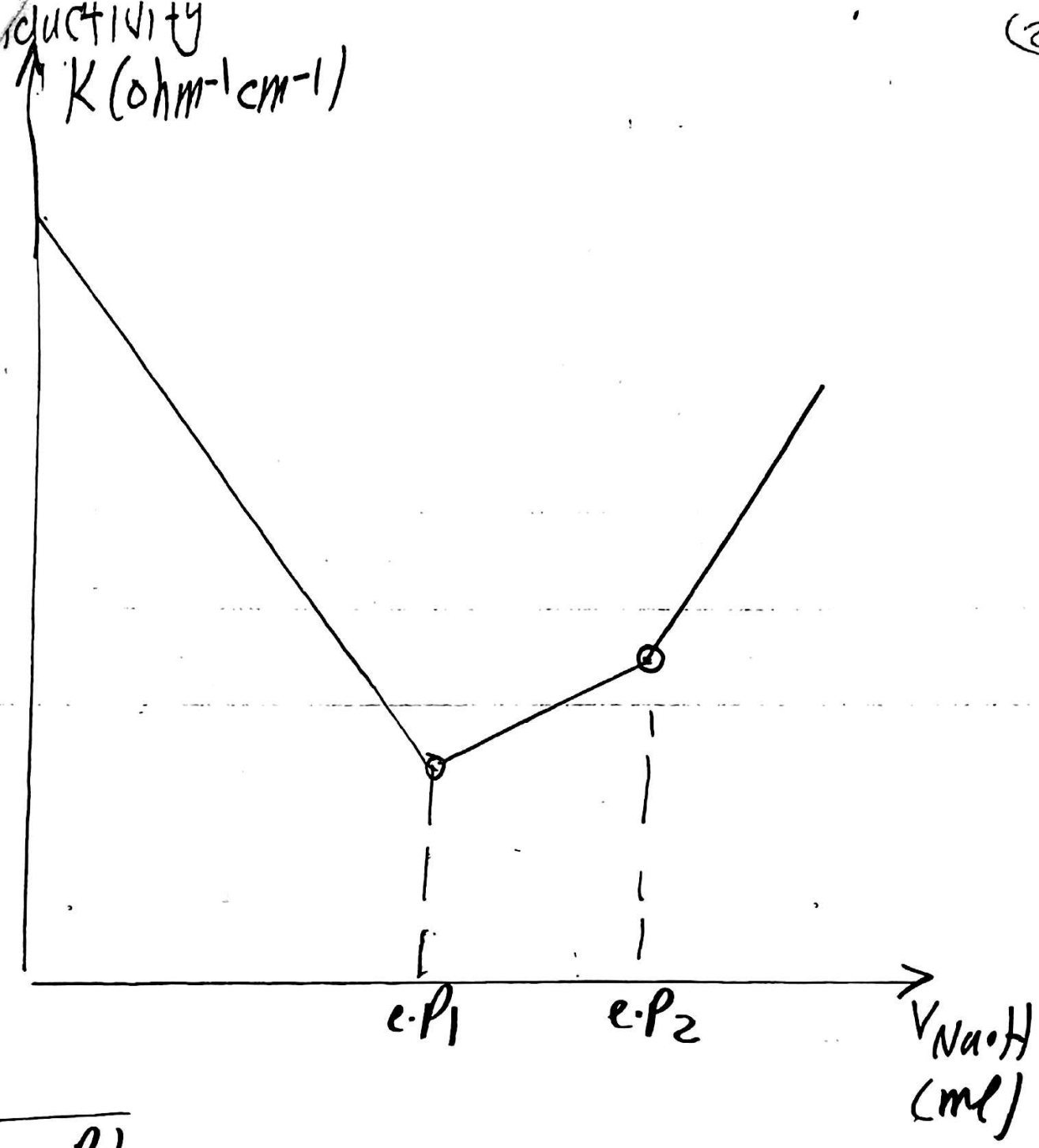

(at e.P1)

$(MV)_{NaOH} = (M.V)_{HCl}$

$0.1 \times e.P_1 = M \times 10$

$M_{HCl} =$ mol/l

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at e.Pt

$(MV)_{NaOH} = (MV)_{HCl} + (M \cdot V)_{CH_3COOH}$

$0.1 \times e.P_2 = \left(\text{(Previous)} \times 10\right)_{HCl} + (M \times 10)_{CH_3COOH}$

M_{CH_3COOH} = mol/l

Table

V_{NaOH}	K/ohm^{-1}(m^{-1})
0 ml	✓
1 ml	✓
2 ml	✓
3 ml	✓
4 ml	✓
⋮	
40 ml	✓

Finsheet

(20)

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Determine Normality Hcl by using 0.1 M NaoH

① Add 25 ml Hcl + 75 ml dist H2O in conical.
② Measure Conductivity.
③ then add 1 ml NaoH and measure Conductivity
④ Add NaoH till 40 ml then finished experiment.
⑤ Draw curve then Det Normality.

Rohrdail	Vnaoh
✓	0
✓	1
✓	2
✓	3 ml
✓	4
✓	5
✓	40

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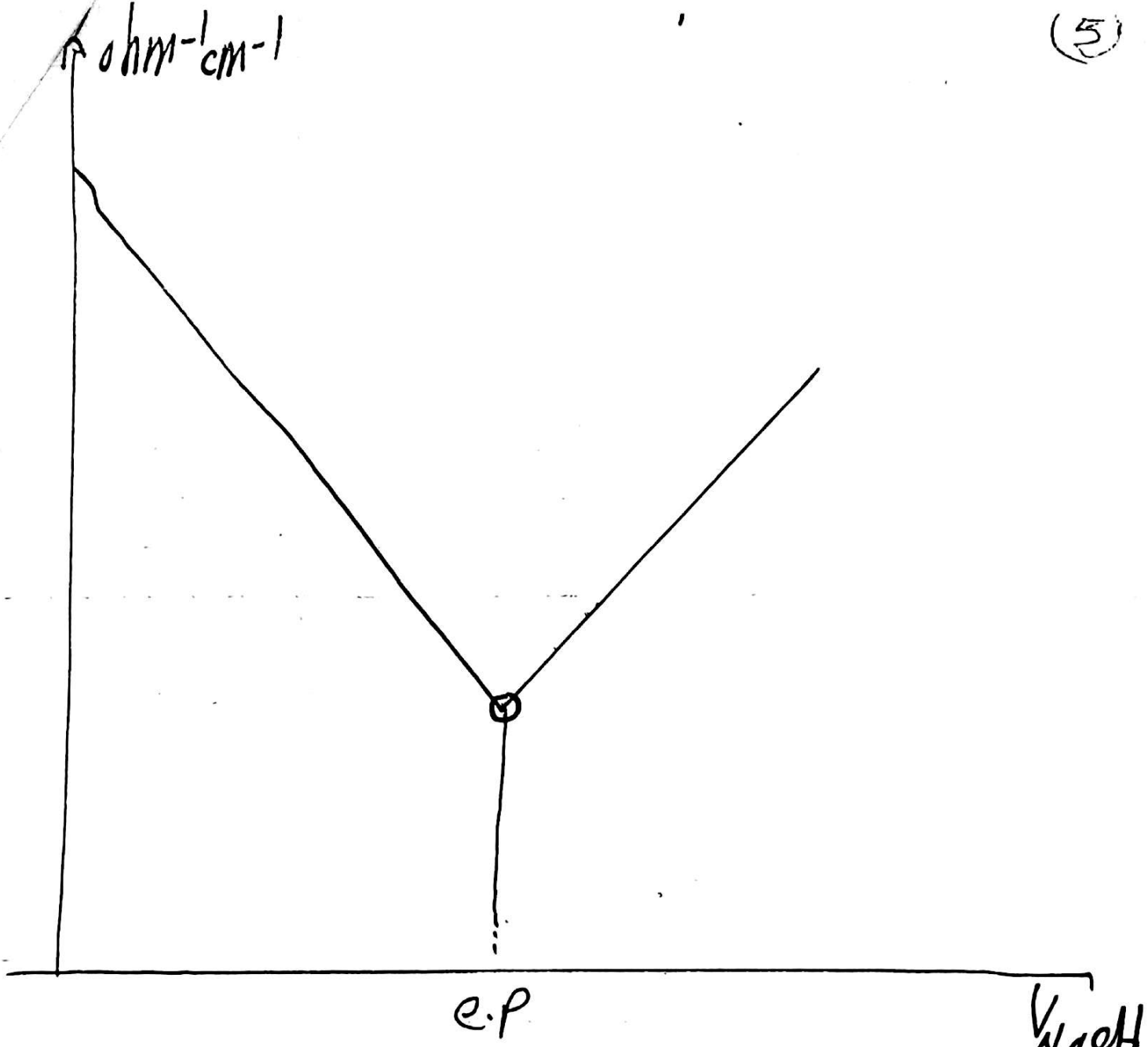


$(MV)_{HCl} = (MV)_{NaOH}$

$M \times 25 = 0.1 \times e.p$

M_{HCl} = mol/l

Note if NaOH by Normality **$(NV)_{HCl} = (N.V)_{NaOH}$**

(2)

/EXP2/

Det Normality of H_3PO_4 by using Potentiometric Method

① Add 25 ml of H_3PO_4 + 75 ml dist H_2O

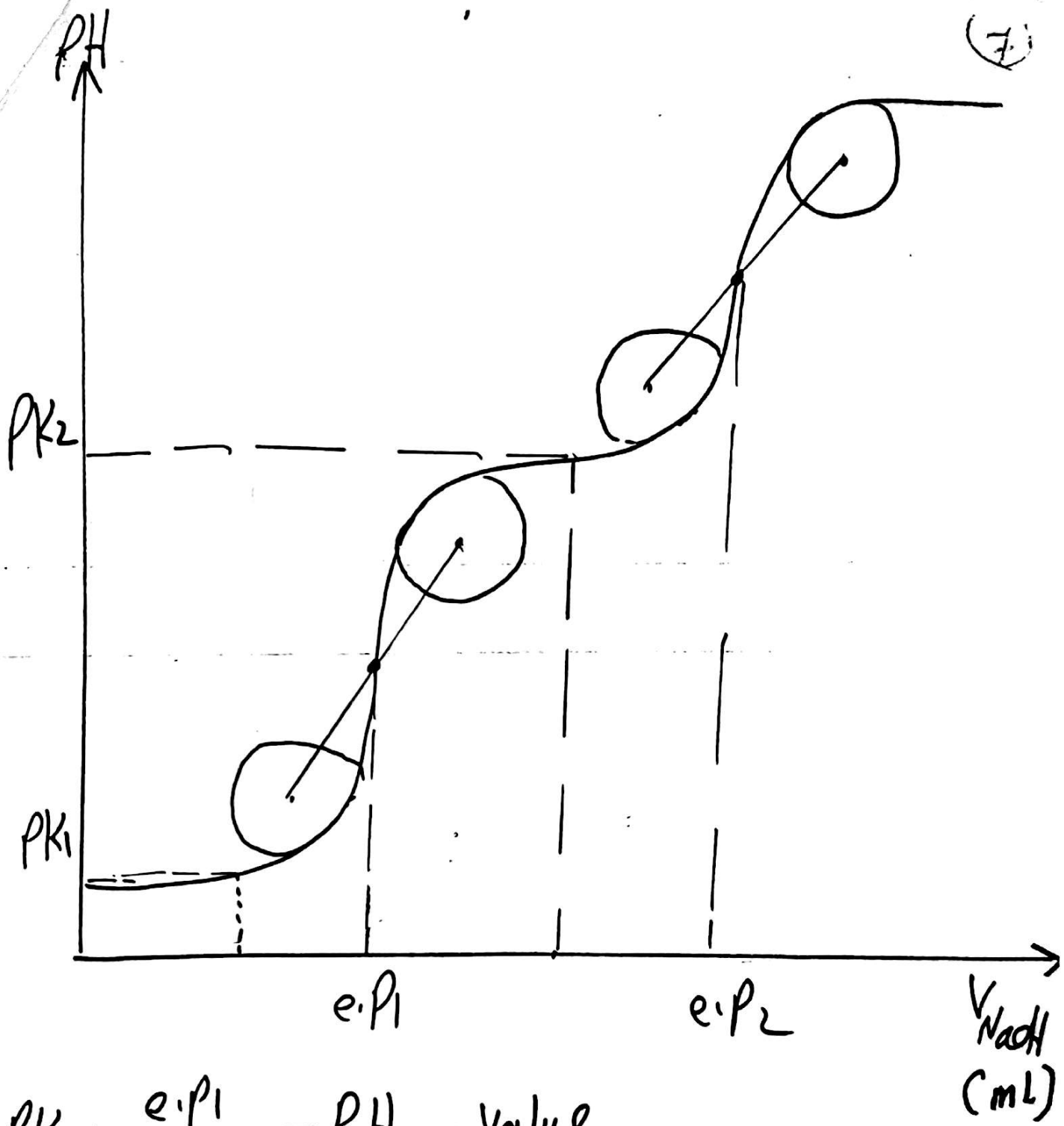
② Measure the PH-meter.

③ Add 1ml 從 [NaoH] from burette then Measure the PH-Meteric.

④ Add ml of NaoH then PH equals /11/.

⑤ Draw the curves then Det Normality.

V_{NaoH}	PH
0	PH_1
1 ml	PH_2
2ml	PH_3
3ml	PH_4
4 ml	PH_5
↓	PH=11



$$PK_1 = \frac{e.P_1}{2} = PH_1 = \text{Value}$$

$$\boxed{K_1 = \log^{-1}(-\text{Value})} \quad mol\,L^{-1}$$

$$PK_2 = \frac{e.P_1 + e.P_2}{2} = PH_2 = \text{Value}$$

$$\boxed{K_2 = \log^{-1}(-\text{Value})} \quad mol\,L^{-1}$$

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pK_1 from 2 ⟶ 2.8

pK_2 from 6.5 ⟶ 7.2

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at e.p1 if NaoH by Molarity

$(MV)_{NaoH} = (M_1 \cdot V)_{H_3PO_4}$

$0.1 \times e.p_1 = M \times 25$

$M_{H_3PO_4} = \ldots$ mol/L

ate e.p2

$(MV)_{NaoH} = 2(M_2 V)_{H_3PO_4}$

$0.1 \times e.p_2 = 2(M \times 28)$

$M_2 H_3PO_4 =$ mol/L

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$M_1 \cong M_2$

If NaOH by Normality

at e.P1

$(N \cdot V)_{NaOH} = \frac{1}{3}(N \cdot V)_{H_3PO_4}$

$0.1 \times e.P_1 = \frac{1}{3}(N_1 \times 25)$

$N_1 H_3PO_4 = \ldots$ gram. eqwt/l

at e.P2

$(NV)_{NaOH} = \frac{2}{3}(N \cdot V)_{H_3PO_4}$

$0.1 \times e.P_2 = \frac{2}{3}(N_2 \times 25)$

$N_2 = {}_{H_3PO_4}$ gram. eqwt/l

$N_1 \equiv N_2$

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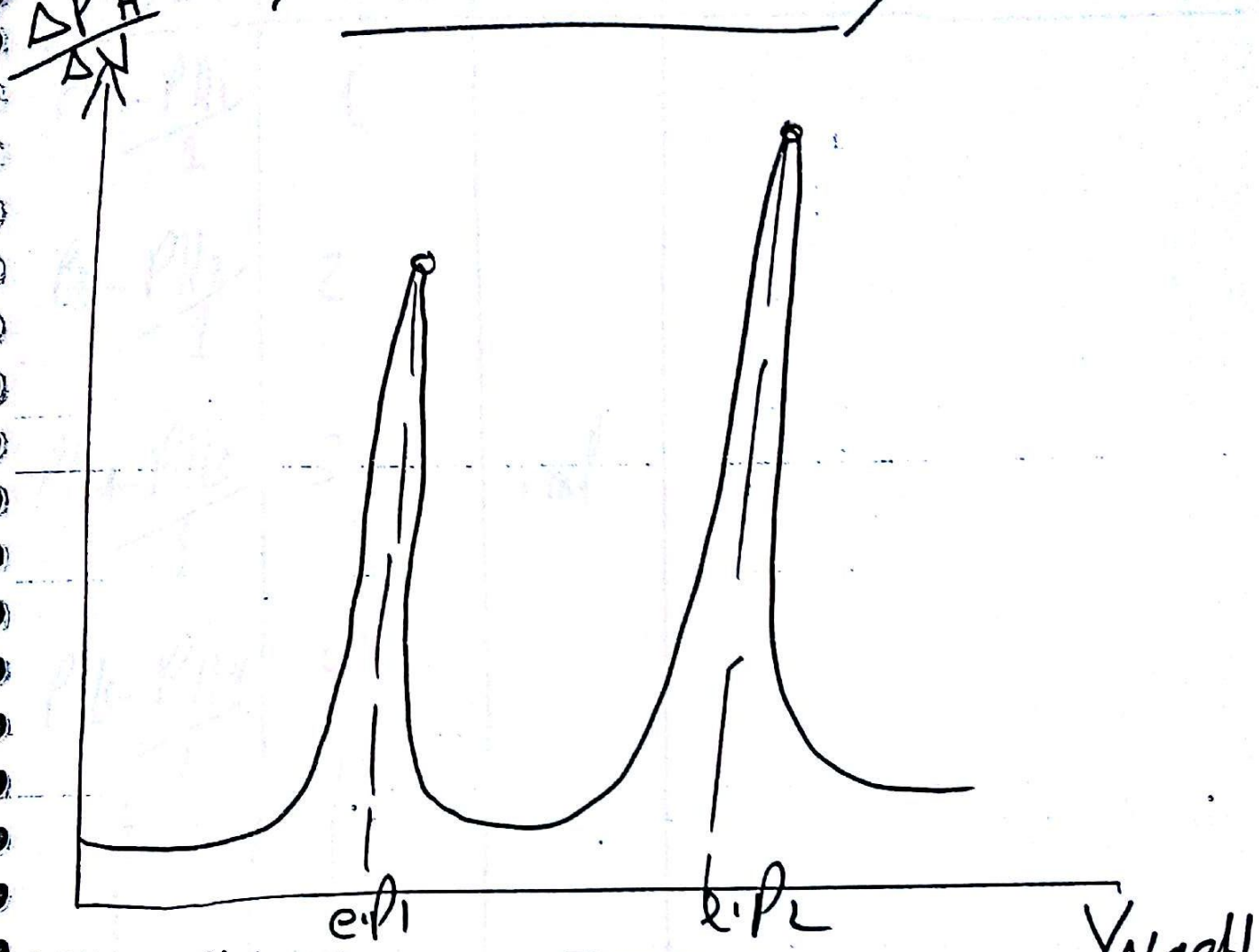
The second curve



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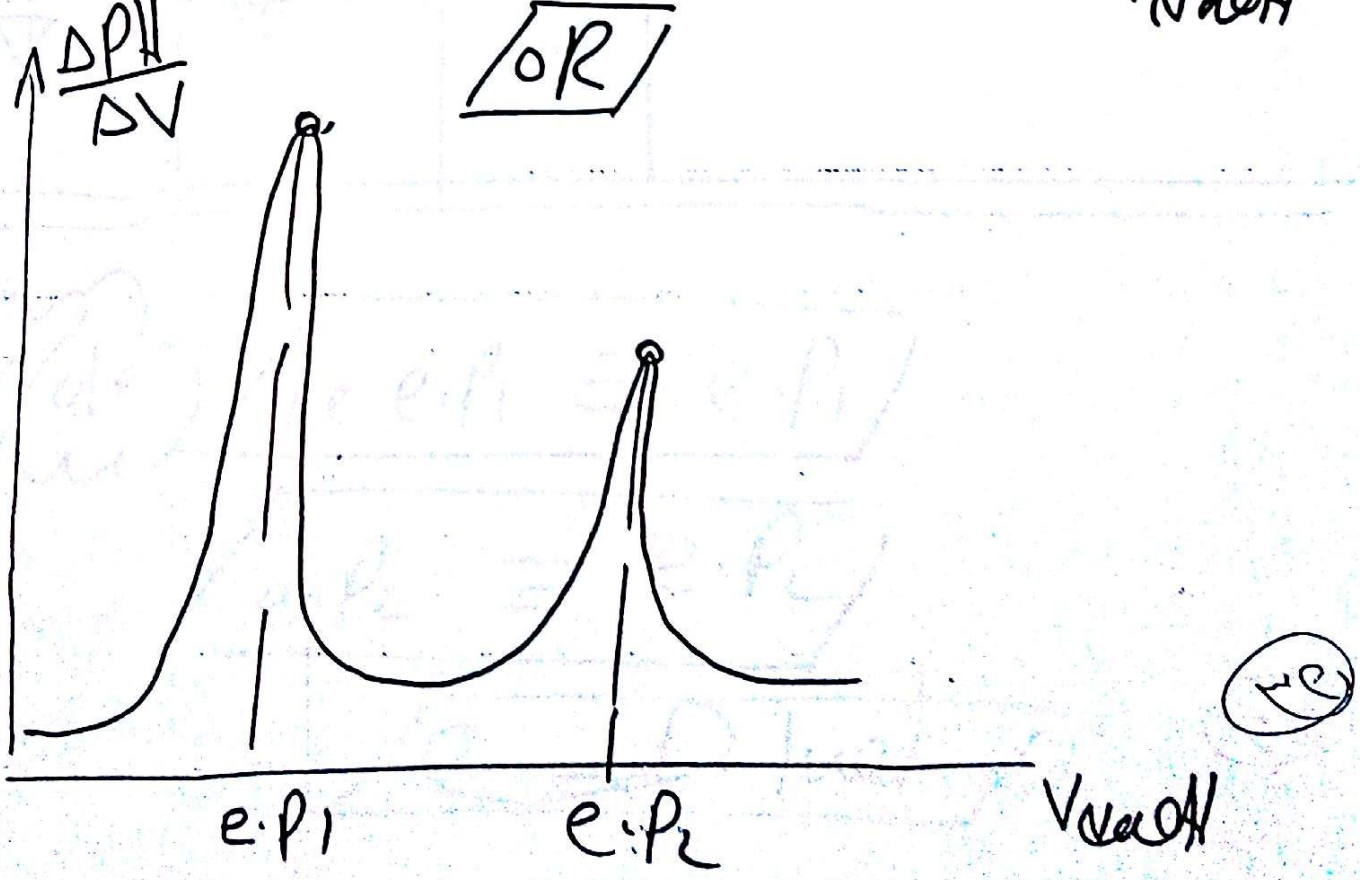

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$\Delta PH/\Delta V$	V_{NaOH}	ΔV
$\frac{PH_2 - PH_1}{1}$	1	
$\frac{PH_3 - PH_2}{1}$	2	
$\frac{PH_4 - PH_3}{1}$	3	1 ml
$\frac{PH_5 - PH_4}{1}$	4	
⋮	⋮	

Note The e.P$_1$ ≡ e.P$_1$

e.P$_2$ ≡ e.P$_2$

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(EXP3)

Determine C_1, C_2 of mixture ($KMnO_4$, $K_2Cr_2O_7$) spectrophotometrically

1. the stock of $KMnO_4$ (6.1×10^{-3} M) and $K_2Cr_2O_7$ (0.1 M) is prepared already.
2. Dilute the solution ($1 - 9 \times 10^{-5}$) and ($1 - 9 \times 10^{-3}$) for $KMnO_4$, $K_2Cr_2O_7$ respectively.
3. prepared 5ml stock add to 5ml stock of $KMnO_4$, $K_2Cr_2O_7$ then complete by 1cm dist H_2O by Measuring flask.
4. Measure the all conc of $KMnO_4$ at $\lambda = 520$ n.m and $K_2Cr_2O_7$ also at $\lambda = 258$ n.m and Measure the Mixture at $\lambda = 528$ n.m
5. Measure all conc of $KMnO_4$, $K_2Cr_2O_7$, mix at $\lambda = 490$ n.m.

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KMnO4

Conc	dilute	Absorbance	λmax
1×10^{-5}	$1\times10^{-3}\times V = 1\times10^{-5}\times25$	A ↙	
3×10^{-5}	$10^{-3}\times V = 3\times10^{-3}\times25$	↙	520 n.m
5×10^{-5}	$10^{-3}\times V = 5\times10^{-5}\times25$	↙	then Measure
7×10^{-5}	$10^{-3}\times V = 7\times10^{-5}\times25$	↙	at 490 n.m
9×10^{-5}	$10^{-3}\times V = 9\times10^{-5}\times25$	↙	

Note before measure must make blank by dist H_2O ($A=0$, $T=100\%$).

Note also Measure the Mixture at 490 n.m and 520 n.m

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$K_2Cr_2O_7$

Conc	dilute	Absorbance	λmax
1×10^{-3}	$0.1 \times V = 1 \times 10^{-3} \times 25$	✓	
3×10^{-3}	$0.1 \times V = 1 \times 10^{-3} \times 25$	✓	at 520 n·m
5×10^{-3}	$0.1 \times V = 1 \times 10^{-3} \times 25$	✓	then 490 n·m
7×10^{-3}	$0.1 \times V = 1 \times 10^{-3} \times 25$	✓	
9×10^{-3}	$0.1 \times V = 1 \times 10^{-3} \times 25$	✓	

Note all this Conc and Volume will be give in exam by Demonstrator

Good luck

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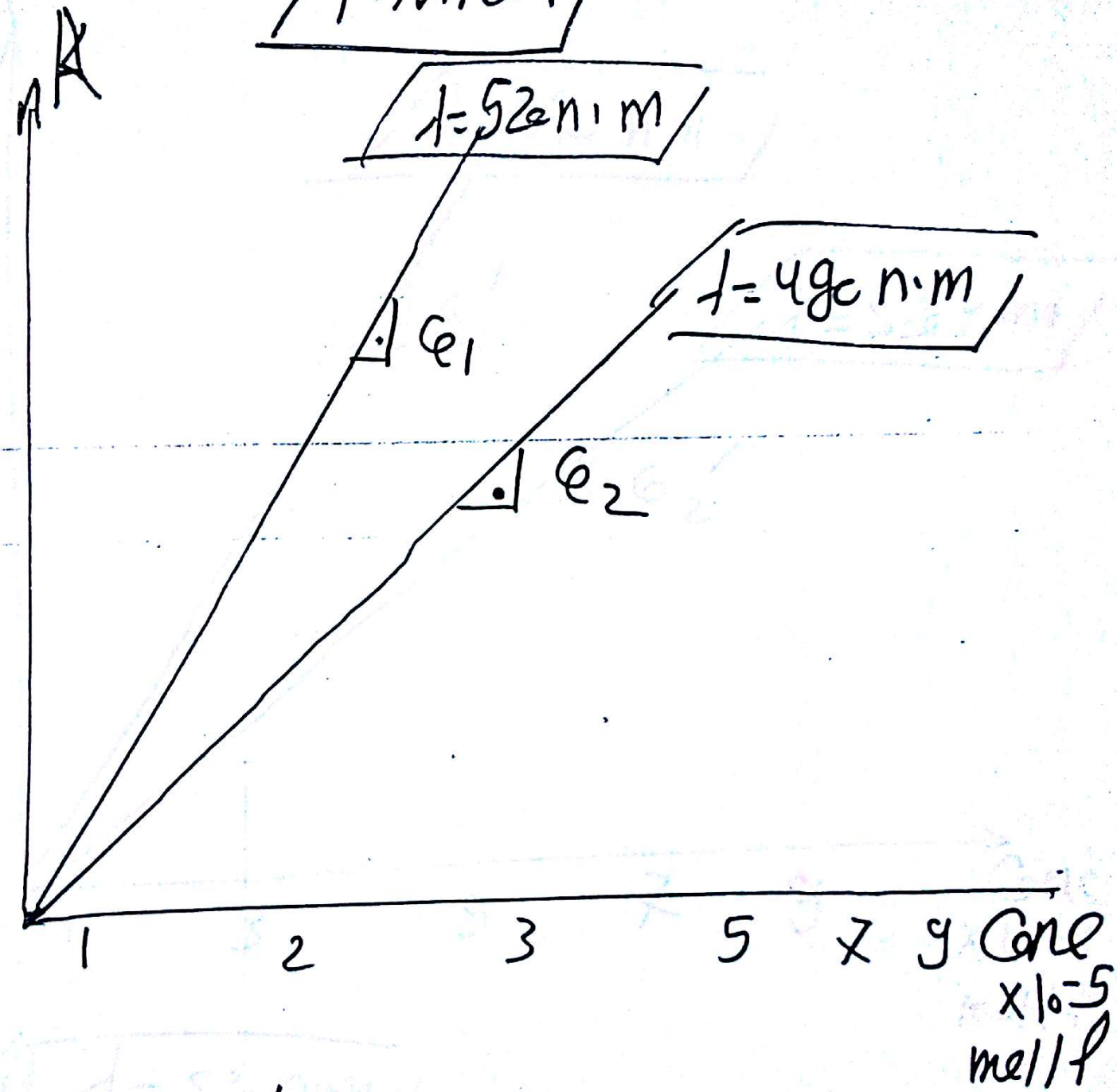
KMnO4



ε_1 : $mol^{-1} l cm^{-1}$

ε_2 : $mol^{-1} l cm^{-1}$

A: Dimensionless

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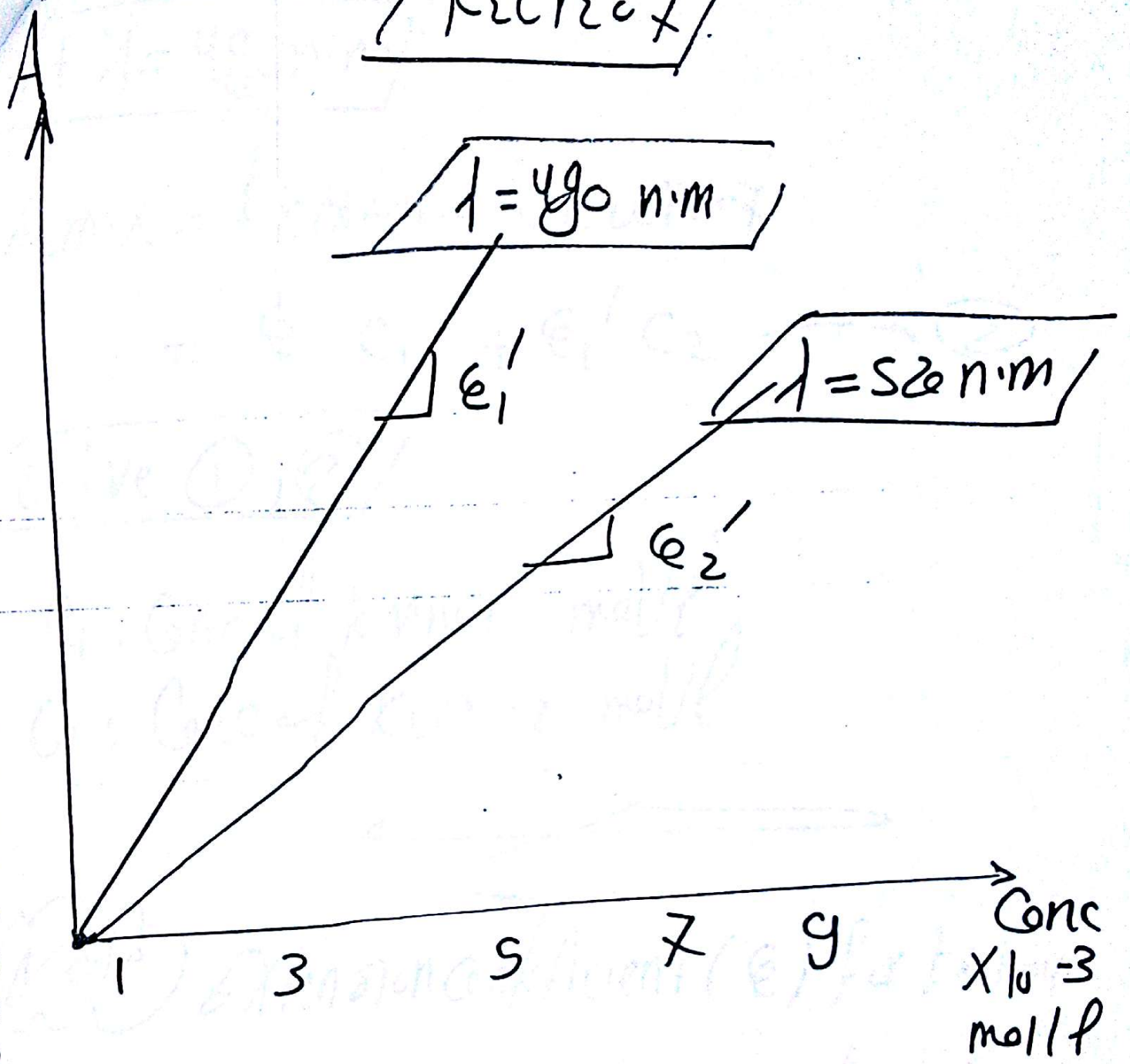
$K_2Cr_2O_7$



at λ = 520 n·m

$A_{mix} = A_{KMnO_4} + A_{K_2Cr_2O_7}$

$\checkmark = \epsilon c_1 + \epsilon c_2$

$\checkmark = \epsilon_1 c_1 + \epsilon_2' c_2$ ——→ (1)

(21)

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at $l = 4\,cm$

$$A_{mix} = A_{KMnO_4} + A_{K_2Cr_2O_7}$$

$$= \epsilon_2 c_1 + \epsilon_1' c_2 \longrightarrow (2)$$

Solve (1), (2)

c_1 : Conc of $KMnO_4$ mol/l

c_2 : Conc of $K_2Cr_2O_7$ mol/l

Note: Extension coefficient (ϵ) for $KMnO_4$

from $g_{cc} \longrightarrow 2000\ mol^{-1}\,l\,cm^{-1}$

Note: ϵ for $K_2Cr_2O_7$

from $50 \longrightarrow 300\ mol^{-1}\,l\,cm^{-1}$

End Mole

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EXP4 / Persulphate and Iodide Reaction /

/1/ affect of Temp /

/A/ Detrmine the observed Rate Constant (K_o)

/B/ Detrmine the true Rate Constant (K_t).

/C/ Detrmine the half life time ($t_{1/2}$).

/D/ Detrmine The Activation Energy (E_a).

/ procedure /

/*/ Determine K_o, K_t, $t_{\frac{1}{2}}$ at Room Temp //25°C/

/1/ take 25 ml of (0.1M KI) in beaker.

/2/ take 25 ml of (0.01 M $K_2S_2O_8$) in another beake

/3/ Pour (بسرعة) KI solution in $K_2S_2O_8$ Solun and start stop watch simultaneously (بالتساوي).

/4/ After (5 minute) take 5ml of mixtures and Add to it 20ml (dist H_2O) + 1ml starch give

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ue Colour.

5/ Titrate with (0.002M $S_2O_3^{-2}$) solun till the blue Colour disappear (Determine Vt).

6/ Repeate this Procedures with (10, 15, 20, 25, 30) min.

(*) Determine V_∞

1/ take the Residue of the mixture and Add to water Bath (حمام مائي) for 30 minutes.

2/ Cool it and then take 5ml of this mixt/ + Comp dist H_2O + 1ml starch. (blue Colour).

3/ Titrate with (0.002M $S_2O_3^{-2}$) till Colorless Then Record V_∞ [one value].

Note The mixture Add to bottles [Residue of mixture] at 60°C for 30 minutes.

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Tables

time (minute)	Vt	V∞	$\frac{V_\infty}{V_\infty - V_t}$	$\ln \frac{V_\infty}{V_\infty - V_t}$
5			—	—
10			—	—
15		one	—	—
20	↓ increase	Value	—	—
25			—	—
30			—	—

Note في حساب Vt ← عند وضع الماء المقطر (2ml) على (5ml mix) نسجل الزمن

Note the Water Make Quenching of Reaction

Note $V_\infty > V_t$ at 30 minute.

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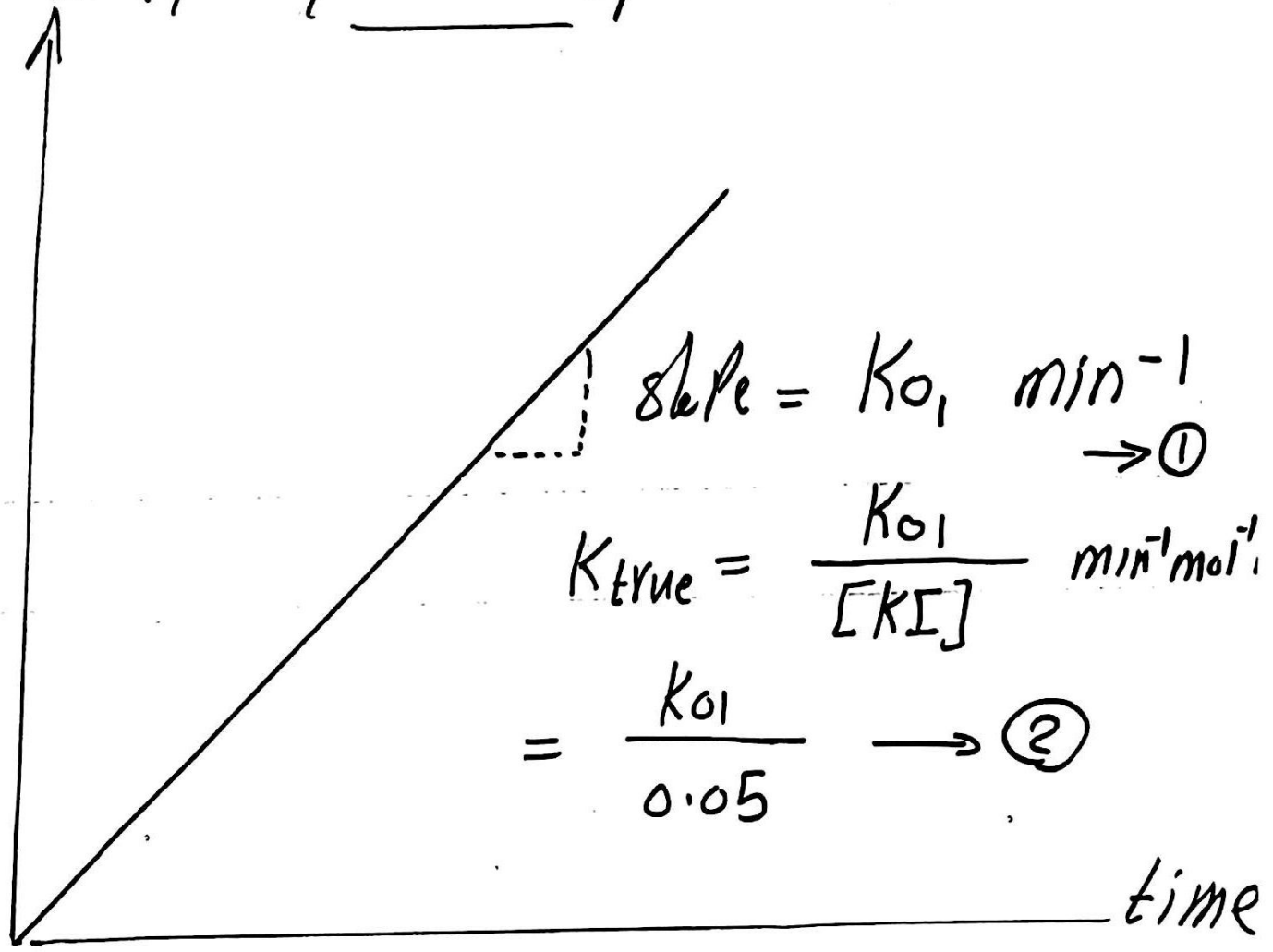
$\ln \frac{V_\infty}{V_\infty - V_t}$ / Curves /



slope = K_{o1} min^{-1} ⟶ ①

$K_{true} = \frac{K_{o1}}{[KI]} = \frac{K_{o1}}{0.05}$ ⟶ ②

$t_{\frac{1}{2}} = \frac{\ln 2}{K_{o1}}$ ⟶ ③

Note the conc of KI = 0.05 due to

$0.1 \times 25 = [KI] \times 50$

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[*] Det K_o, K_t, $t_{\frac{1}{2}}$ at high Temp (40°c)

[1] Take 25 ml of 0.1 M KI in beaker. and R bottle.
[2] take 25ml of 0.01 M $K_2S_2O_8$ in another beaker
[3] Put two bottles in water Bath to raise it's Temp to 40°c using thermostate.
[4] until the two bottles reach to 40°c Pour the KI solun to $S_2O_8^{-2}$ and start Stop Watch.
[5] After 5 minute take 5ml of mixture + 2ml dist.H2O + 1ml starch. (blue colour).
[6] titrate with $Na_2S_2O_3$ till Colorless (Determine Vt and 5 minute).
[7] Repeate steps as previous (10, 15, 20, 25, 30 minute).

Note the Reaction mix must be mentain at Const Temp 40°c during Reaction.

عند سحب 5ml من الخليط توزع يكون عند درجة حرارة 40°c .